

Highly-ordered Metal-modified Mesoporous Carbon Nitride: As a Novel Hydrogen Adsorbent

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In this study, ordered mesoporous carbon nitride with high surface area and pore volume has been synthesized through a simple polymerization reaction between ethylene diamine and carbon tetrachloride in mesoporous silica media, and modified by Ni doping. The mesoporous carbon materials have been characterized by BET surface area and XRD analysis (low and wide angle). Adsorption data of H_2 on the mesoporous carbons were collected with PCT method for a pressure range up to 100 bar at 303 K. The effect of nickel doping and carbon-nitrogen (C-N) structure on hydrogen adsorption capacities was investigated. The amount of hydrogen adsorbed on nickel-doped mesoporous carbon nitride (Ni-MCN, 1.49 wt. %) and nickel-doped mesoporous carbon (Ni-MC, 1.24 wt. %) in contrast with mesoporous carbon nitride (MCN, 1 wt. %) and pristine mesoporous carbon (MC, 0.83 wt. %) has been enhanced.

Key words:

mesoporous carbon nitride, nickel, surface modification, hydrogen storage

Introduction

Development of hydrogen-fueled vehicles can bring economic and environmental benefits through decreased use of oil, and, consequently, a decrease in air pollution and other greenhouse gases.¹ However, one of the most important drawbacks of the use of hydrogen as a fuel is that it has to be stored. There are different techniques to store hydrogen. All those techniques have to meet the provisional criterion of the Department of Energy of the United States (DOE). The DOE has established different targets for onboard hydrogen storage systems, including the minimum “gravimetric” and “volumetric” capacity and the reversibility of the charging/discharging processes. For the year 2010, the storage system had to have a gravimetric capacity of 2 kWh kg⁻¹ (6 wt. % of H_2) and a volumetric capacity of 1.5 kWh L⁻¹ (0.045 kg H_2 L⁻¹). In the case of the European Hydrogen & Fuel Cell Technology Platform, it requested energy density values of 1.1 kWh L⁻¹ in its Strategic Research Agenda (SRA) and Deployment Strategy (DS) documents, published at the end of 2004, and reviewed in 2005.² These energy density values are equivalent to a volumetric hydrogen storage capacity of about 33 g H_2 L⁻¹. It is important to note that, in the case of materials-based technologies, to achieve system-level capacities, the gravimetric and volumetric capacities of the materi-

al alone must clearly be higher than the system-level targets (depending on the material and the system design, material capacities may need to be higher by a factor of 1.2–2 times than system capacity targets³). These values are referred to the whole system, including the storage medium, the vessel, the refueling infrastructure, any regulators, electronic controllers, sensors, and so on.

Recently, mesoporous carbons with well-ordered pore systems offered great potential in hydrogen storage.^{4–7} The carbons were obtained via the template method, which involved the introduction of suitable carbon precursors into the ordered pores of the template, followed by carbonization, and finally, removal of the template.^{8–10} These carbon materials usually have large specific surface areas and high pore volumes, which are useful for effective physisorption of H_2 . Besides, the ordered networks may provide fast transportation in the materials, a noticeable volume of micropores can efficiently adsorb hydrogen, and the micro- and the mesoporosity can be adjusted by changing the template, the carbon precursor, and the amount of carbon infiltrated in the template.¹¹ In fact, hydrogen adsorption on carbon materials is strongly ascribed to surface heterogeneity, depending in its turn on their preparation and formulation. Surface heterogeneity can arise not only from surface irregularities, including bound impurities and functional groups, but also from nanopore polydispersity (structural heterogeneity).

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Recently, a hydrogen spillover effect was successfully used in hydrogen storage media based on physisorption, such as carbon materials,^{12,13} zeolites,¹⁴ MOFs^{15,16} by Ralph T. Yang and coworkers. It was observed that the hydrogen storage capacity of nanostructured materials could be greatly enhanced by doping them with metal-supported catalysts through a carbon bridge. The increased hydrogen storage capacity of catalyst-doped porous materials is attributed to the hydrogen spillover effect. The process includes a dissociation of hydrogen molecules on a metal and subsequent spillover to its support, while the carbon bridge helps the hydrogen to spillover to the target porous materials that formed the secondary spillover. This process modifies the chemical nature of the porous materials and activates the porous materials to strengthen subsequent hydrogen physisorption.¹⁷

In this work, the influence of the texture and surface chemistry of mesoporous carbon molecular sieve were systematically studied in hydrogen storage. We prepared nickel-modified mesoporous carbon nitride and investigated the effects of specific surface area and surface functional group (nitride and nickel functional groups) on hydrogen uptake. Herein, the H_2 sorption densities of the materials were measured at 303 K over the hydrogen pressure range up to 100 bar.

Experimental

Materials

The reactants used in this study were tetraethyl orthosilicate (TEOS) as a silica source, cetyltrimethylammonium bromide (CTAB) as a surfactant, sodium hydroxide (NaOH), sodium fluoride (NaF), and deionized water for synthesis of mesoporous silica (MCM-48), sucrose as a carbon source, and sulfuric acid as a catalyst for synthesis of mesoporous carbon, EDA (ethylene diamine) and CTC (carbon tetrachloride) for synthesis of mesoporous carbon nitride (MCN). All the chemicals were of analytical grade and purchased from Merck.

Experimental procedure

Synthesis of mesoporous silica (MCM-48)

MCM-48 was prepared according to the synthesis procedure described by Shao.¹⁸ In a representative synthesis, the MCM-48 molecular sieves were prepared as follows: 10 mL of tetraethyl orthosilicate (TEOS) was mixed with 50 mL of deionized water, and the mixture was vigorously stirred for 40 minutes at 333 K, then 0.9 g of NaOH was added into the mixture, and at the same time, 0.19 g of NaF was added into the mixture. After the NaF

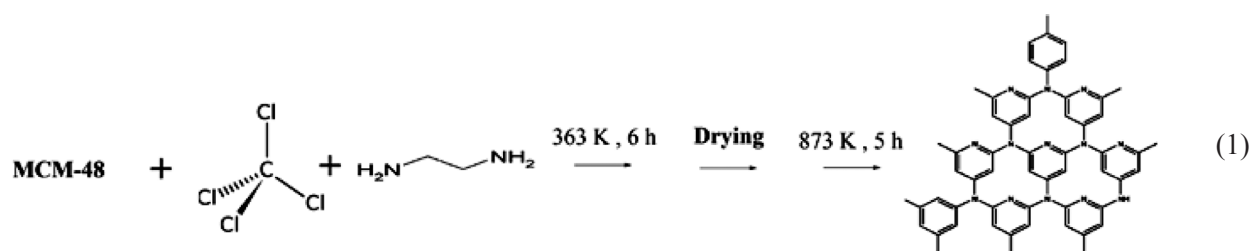
was added completely, the required content of sources, respectively, were added. After another 60 minutes of vigorous stirring, 10.61 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture, and stirring continued for 60 minutes. The mixture was heated for 24 h at 393 K in an autoclave under static conditions, and the resulting product was filtered, washed with distilled water, and dried at 373 K. The as-synthesized samples were then calcined in air for 4 h at 848 K, increasing the temperature to 848 K at 1 K min⁻¹ of the heating rate.

Synthesis of mesoporous carbon (MC)

MC was prepared according to the synthesis procedure described by Ryoo.⁸ In a representative synthesis, the MC molecular sieve was prepared as follows: 1.25 g sucrose and 0.14 g H_2SO_4 in 5.0 g H_2O was dissolved, and this solution was added to 1 g MCM-48. The sucrose solution corresponded approximately to the maximum amount of sucrose and sulfuric acid that could be contained in the pores of 1 g MCM-48. The resultant mixture was dried in an oven at 373 K, and subsequently, the oven temperature was increased to 433 K. After 6 h at 433 K, the MCM-48 silica containing the partially carbonizing organic masses was added with an aqueous solution consisting of 0.75 g sucrose, 0.08 g H_2SO_4 and 5.0 g H_2O . The resultant mixture was dried again at 373 K, and subsequently, the oven temperature was increased to 433 K. The color of the sample turned very dark brown or nearly black. This powder sample was heated to 1173 K under vacuum using a fused quartz reactor equipped with a fritted disk. The carbon-silica composite thus obtained was washed with 1 mol L⁻¹ NaOH solution of 50 % ethanol- 50 % H_2O twice at 363 K, in order to dissolve the silica template completely. The carbon samples obtained after the silica removal were filtered and washed with ethanol and dried at 393 K.

Synthesis of mesoporous carbon nitride (MCN)

Mesoporous carbon nitride materials were prepared by using mesoporous silica MCM-48 as template. In a typical synthesis (as shown in Eq. 1), 0.5 g of calcined MCM-48 was added to a mixture of EDA (1.35 g) and CTC (3 g). The resultant mixture was refluxed and stirred at 363 K for 6 hours. Then, the obtained dark brown solid mixture was placed into a drying oven for 12 hours, and ground into fine powder. The template-carbon nitride polymer composites were then heat-treated in a nitrogen flow of 50 mL per minute at 873 K with the heating rate of 3 K min⁻¹ and kept under these conditions for 5 h to carbonize the polymer. The mesoporous



carbon nitride was recovered after dissolution of the silica framework in 5 wt. % hydrofluoric acid, by filtration, washed several times with ethanol, and dried at 100 °C.

Nickel-doped samples

The mesoporous carbon samples were impregnated with nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) acetone solutions by a vacuum decomposition process using the incipient wetness impregnation method.¹⁹ In this study, a nickel nitrate solution (analytical grade) of a low concentration (5 mmol L^{-1}) was selected for the vacuum impregnation process in 3 hours. Mesoporous carbon impregnated with the acetone solution was then filtered and dried at 60 °C for 4 h. The resultant mesoporous carbon doped with Ni was then heated at 100 °C for 1 h under hydrogen atmosphere to reduce the nickel salt to nanoparticles. The activation temperature was 1033 K and optimum N_2 gas flow rates (250 mL min^{-1}) were used.²⁰

Characterization

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu K α radiation. The diffractograms were recorded in the 2θ range of 0.8–10 with a 2θ step size of 0.01° and a step time of ones.

Adsorption-desorption isotherm of the as-synthesized sample was measured at 77 K on a Micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method while Bruner-Emmet-Teller (BET) measured surface area of the sample. Transmission electron microscopy was carried out using a Philips CM30 instrument operating at 300 kV in the bright field mode. For that, the samples were crushed in acetone and dispersed on a holey carbon grid. A Shimadzu XPS (AXIS-HS type) was employed to measure changes in surface functional groups before and after surface modification. The AlK α line was used as the exciting X-ray source (1486.6 eV). Thermal analysis was carried out by means of NETZSCH STA449C analyzer. The tool settings were: heating rate 10 °C min^{-1} and an air atmo-

sphere with 100 mL min^{-1} flow rate. For each measurement, about 25 mg of a ground adsorbent sample were used. From the weight loss curve, the differential weight loss was calculated where peaks represent the weight loss.

Hydrogen adsorption

Hydrogen adsorption capacities at 303 K over the hydrogen pressure range up to 100 bar were measured by the PCT method (AnySorb 7) with an automatically controlled apparatus for high-pressure adsorption. The hydrogen adsorption capacities were measured after all samples had been pretreated at 423 K for 90 minutes in helium flow, and sequentially reduced in situ in a hydrogen/nitrogen mixture flow. The dead volume was calibrated with helium gas at room temperature. High-purity hydrogen (99.999 %) was used in this study. The amounts of hydrogen adsorbed were calculated using the Redlich/Kwong equation. Steps were taken to ensure the accuracy of the experimental results. The principal part of the apparatus was held in an air thermostat to keep its temperature at 303 K. The apparatus was previously tested for leakage and calibrated with the empty sample cell and well-known standard samples. The time adopted for equilibration was 30 minutes at each step. About 300 mg of the mesoporous carbon samples were used for hydrogen adsorption.

Results and discussion

Textural characterization

As shown in Fig. 1, all mesoporous carbon samples show type IV isotherms with obvious hysteresis loops, indicating that mesoporous carbon samples are typical mesoporous materials. It can also be seen from the inset in Fig. 1 that the pore sizes of MC, MCN, Ni-MC and Ni-MCN locate in mesopore size range, and their most probable pore diameters are 4.6, 4.1, 4.4 and 3.9 nm, respectively. From the nitrogen sorption isotherms of mesoporous carbons before and after chemical modification, it can be seen that, after chemical modification, the obtained carbons still have type IV

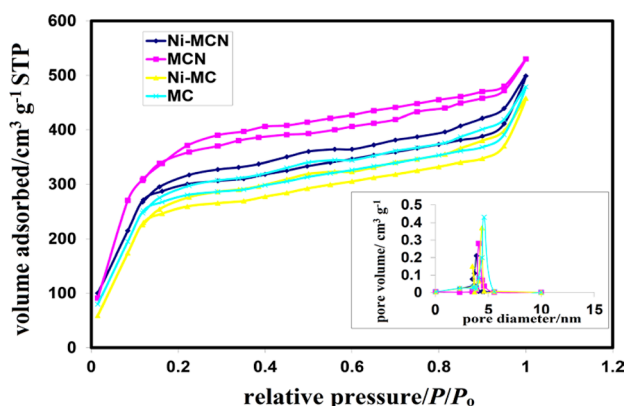


Fig. 1 – Adsorption-desorption isotherms of nitrogen at 77 K on MC, Ni-MC, MCN and Ni-MCN. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm

isotherms, indicating that mesoporosity is preserved. The textural parameters listed in Table 1 clearly confirm the structural changes of modified and unmodified mesoporous carbon samples.

Table 1 – Textural parameters of the MC, Ni-MC, MCN and Ni-MCN employed in this study

Adsorbent	Pore size (nm)	A_{BET} ($\text{m}^2 \text{g}^{-1}$ total)	A_{BET} ($\text{m}^2 \text{g}^{-1}$ carbon)	V ($\text{cm}^3 \text{g}^{-1}$ total)
MC	4.6	1530		0.73
Ni-MC	4.4	1501	1709	0.69
MCN	4.1	1510		0.71
Ni-MCN	3.9	1481	1743	0.64

In order to check the structural degradation, XRD data of carbonaceous adsorbents were obtained on Philips 1830 diffractometer using Cu K α radiation of wavelength 0.154 nm. Fig. 2 reports low angle XRD patterns of the parent mesoporous carbon and of samples MCN, Ni-MC and Ni-MCN.

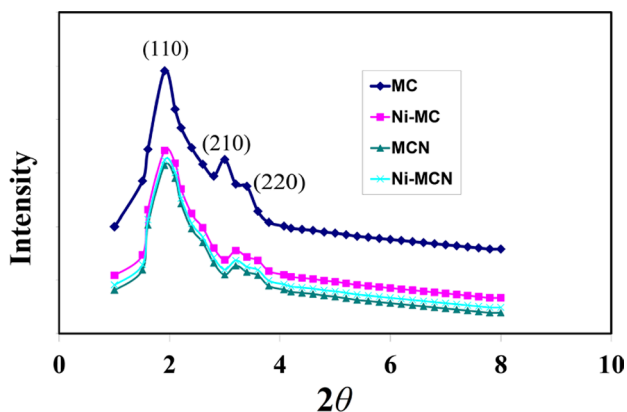


Fig. 2 – XRD pattern of (a) MC (b) Ni-MC (c) MCN (d) Ni-MCN

The XRD patterns of MC showed the two characteristic reflections (211) and (220) in the 2θ range from 0.8° to 10° , indicating a well-ordered cubic pore with all replicas, the main reflection peak is well maintained, representing well-ordered cubic I4132 pores. With respect to the parent silica, a shift of the d100 peak towards higher 2θ values is observed, in agreement with the literature.¹⁸

The wide-angle XRD patterns of nickel-modified mesoporous adsorbents (Ni-MC and Ni-MCN) in Fig. 3 exhibit two resolved diffraction peaks at 44.59° (111) and 51.90° (200) 2θ , characteristic of metallic nickel with a FCC structure. It reveals that the nickel species in the mesoporous carbon matrix exists in metallic form.

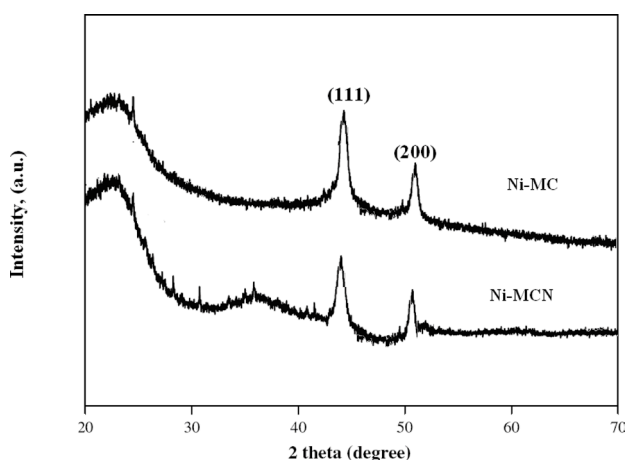


Fig. 3 – Wide-angle XRD patterns of the nickel-modified mesoporous carbon (Ni-MCN) and mesoporous carbon nitride (Ni-MC) adsorbents

TEM images of unmodified ordered mesoporous carbon (MC) and nickel-modified mesoporous adsorbents (Ni-MC and Ni-MCN) are shown in Fig. 4. The TEM image indicates that the metal-modified mesoporous carbon shows a typical well-defined hexagonal symmetry after modification. For Ni-MC and Ni-MCN, it can be seen that the mesoporous carbon structure is preserved but does not have structure that is as well-ordered as pristine-ordered mesoporous carbon. In this case, the nickel was found homogeneously dispersed on the surface of mesoporous carbon and carbon nitride. The particles possess a mean size of about 20–30 nm.

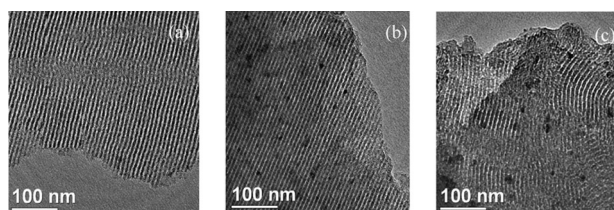


Fig. 4 – TEM images of (a) MC, (b) Ni-MC and (c) Ni-MCN

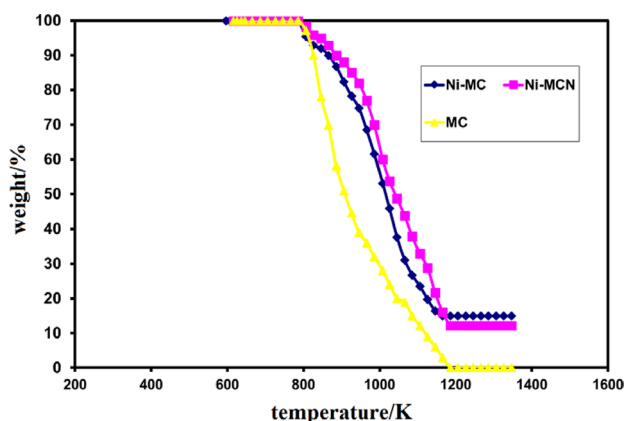


Fig. 5 – Thermogravimetric analysis (TGA) plots of the unmodified and modified mesoporous carbon and nickel-modified mesoporous carbon nitride

Fig. 5 shows thermogravimetric analysis (TGA) curve of MC, Ni-MC and Ni-MCN using a heating rate of 10 K min⁻¹. The Ni-MC and Ni-MCN presented 85 % and 87.8 % weight loss from 800 to 1160 K linked to the oxidation of the carbon. The weight loss is found after oxidation of the mesoporous carbon, which is related to the nickel oxide in the prepared nanocomposite.

Hydrogen adsorption study

We estimated the hydrogen storage capacity of modified mesoporous carbon with the PCT method. Fig. 6 shows hydrogen adsorption isotherms of mesoporous carbons studied over hydrogen pressure up to 100 bar at 303 K. We obtained similarly shaped hydrogen adsorption isotherms in spite of surface modification for mesoporous carbon and mesoporous carbon nitride adsorbents studied. Hydrogen adsorption capacity is a linear function of pressure, which can be explained by Henry's law. These results indicated that nickel was well dispersed on the surface of adsorbents. The amount of adsorbed hydrogen increased with increasing pressure. The amounts of hydrogen adsorbed on nickel-doped mesoporous carbon and mesoporous carbon nitride adsorbents (Ni-MC, Ni-MCN) were much larger than parent mesoporous carbon and mesoporous carbon nitride adsorbent (MC, MCN) respectively. In the data shown in Fig. 6, the effect of activation of nickel is more prominent, and thus led to more hydrogen storage. It could be confirmed that surface modification of mesoporous carbon adsorbents plays an important role in determining the porous structure and amounts of hydrogen adsorbed. As we can see, mesoporous carbon nitride has shown much better hydrogen storage capacity in respect to pristine mesoporous carbon; this is because of the stronger interaction of hydrogen on the carbon-nitrogen skeleton than the simple carbon skeleton.

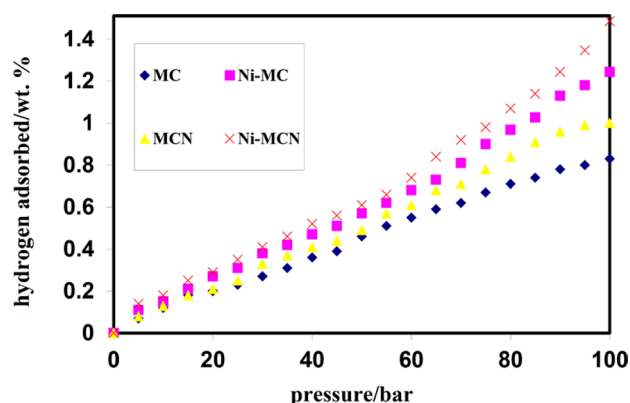


Fig. 6 – Hydrogen adsorption isotherm of the unmodified and nickel-modified mesoporous carbon and mesoporous carbon nitride at 303 K

Fig. 7 shows the effect of specific surface area and surface structure on the hydrogen adsorption capacity of the all mesoporous carbon adsorbents studied at 100 bar, 303 K. In this study, as the specific surface areas of modified mesoporous carbon adsorbents are decreased, their hydrogen adsorption improved as compared with unmodified mesoporous carbon adsorbents due to the enhancement of hydrogen affinity by Ni doping.

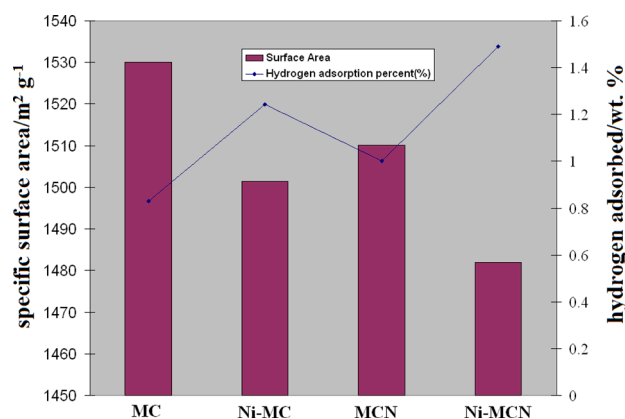


Fig. 7 – Effect of specific surface area and surface structure on the hydrogen adsorption capacity of unmodified and nickel-modified mesoporous carbon and mesoporous carbon nitride adsorbents at 100 bar, 303 K

The present results clearly show the central role of the nickel and carbon nitride structure in the hydrogen uptake for modified and unmodified mesoporous carbon and mesoporous carbon nitride samples. The uptake level is restricted by the pore volume level. In the presence of nickel, the pore volume decreases in the presence of nickel. For a given nickel content, the hydrogen uptake only slightly changes with the nature of the metal precursor because the specific area is almost unchanged. The uptake changes slightly with the temperature of the pre-treatment, probably a result of structural changes in the carbon frame. The excess of hydro-

gen uptake by the nickel nanoparticles as compared to that of the pristine mesoporous carbon and mesoporous carbon nitride can be attributed to a hydrogen adsorption process through a spillover mechanism,^{21,22} namely the dissociation of hydrogen on the metal phase then migration onto the support.

Recently, Yang *et al.*²³ reported that hydrogen-uptake capacity could be remarkably enhanced in the presence of transition metals, because of the spillover of hydrogen molecules into carbon structures. The presence of Ni particles can also encourage the hydrogen uptake of nickel-modified mesoporous carbon and mesoporous carbon nitride by means of hydrogen-molecule spillover.

Finally, it's clear that, on carbon nanostructure sites, at room temperature and high pressure, the hydrogen directly adsorbs from the gas phase. The H-adspecies formed may easily desorb at room temperature and pressure. To summarize, the hydrogen reservoir may originate from two sources: (i) Hydrogen spillover species adsorbed on the carbon support via the nickel phase; (ii) Hydrogen species directly adsorbed from the gas phase onto carbon and nitrogen active sites generated by the H₂ pre-treatment.

Conclusions

In the present work, MCM-48 carbon replicas were synthesized by using a sucrose solution as carbon source. The structural order and textural properties of the modified and unmodified mesoporous adsorbents was studied by XRD and nitrogen adsorption analyses. Enhanced hydrogen adsorption was observed on the carbon adsorbents for surface modification by nickel and for mesoporous carbon nitride structure at hydrogen pressures of about 100 bar, 303 K. The effect of the doping and modifying technique on the hydrogen storage is to help hydrogen molecules dissociate and spill over effectively into the surface and inner surface of the nanostructured carbon materials. Therefore, it should be noted that a good dispersion of the metal-supported catalyst on the mesoporous carbon nitride helps to diffuse effectively, which plays a key role in deciding the final hydrogen storage capacity of Ni-doped mesoporous carbon nitride.

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